Fingerprinting and Forensic Techniques for Landfill Gas Geochemical Assessment

LEA/CIWMB Partnership Conference
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Orange County LEA

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Session Agenda

Theory of Gas Geochemistry

I. Introduction – Stating the Problem
II. Identification of Methane Sources
III. Analytical Procedures/Methods
IV. Data Interpretation Techniques

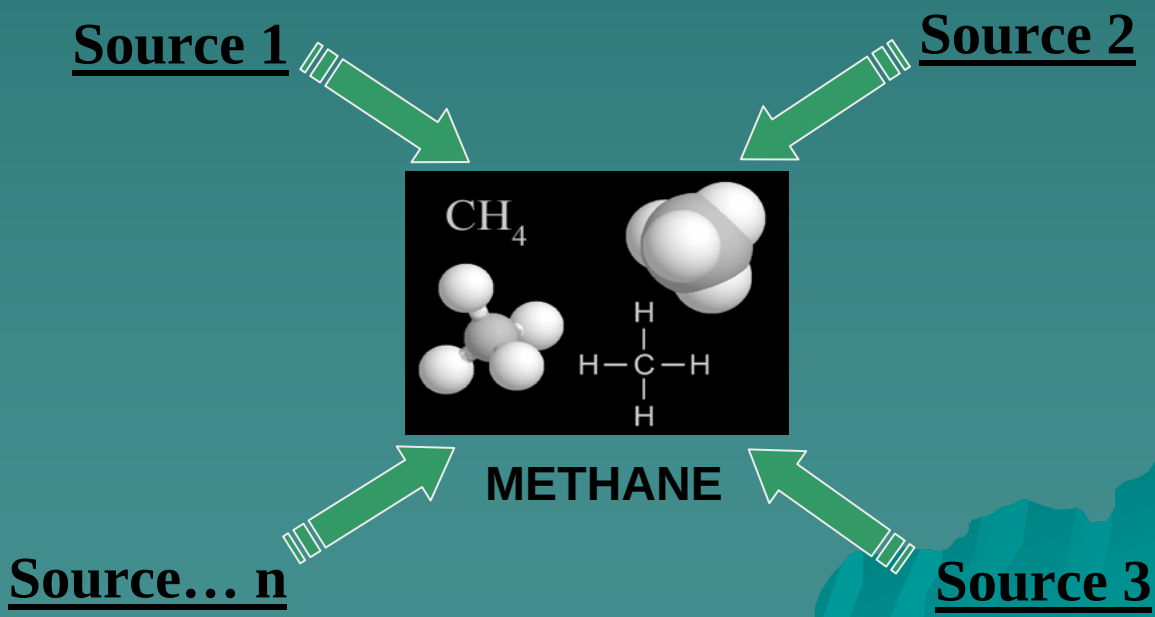
Case Studies in Orange County

Case I (Newport Terrace Landfill – Newport Beach, CA)
Case II (Cannery Street Landfill – Huntington Beach, CA)

V. Background/Description of Case Studies
VI. Workplan Implementation and Procedures
VII. Results and Interpretation
VIII. Conclusions

Questions

I
Introduction
Stating the Problem



Problem Setting

- Methane as greenhouse & explosive gas
- CH_4 Migration/Accumulation = Hazards
- LEA/CIWMB task = Gas Monitoring and Control (27 CCR, Section 20919)

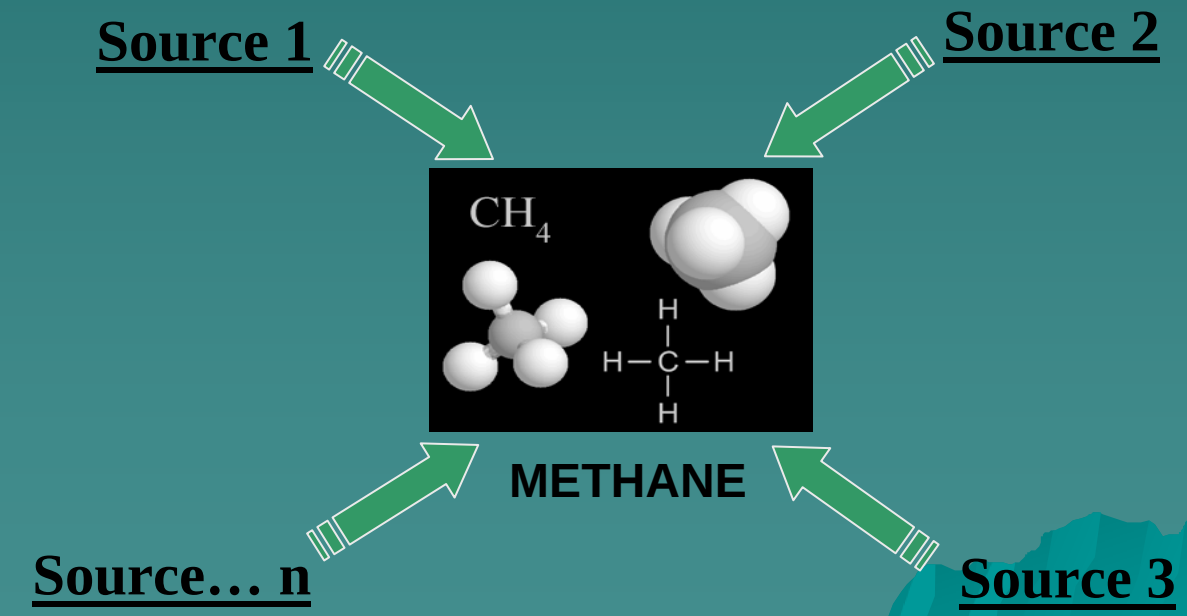
Fugitive methane from **OTHER SOURCES**

Problem Setting (contd.)

Identification and correlation of methane releases to their source

Why?

Scenarios/ Sources?



Why?

- To determine Responsible Parties
- To determine LEA involvement

- Adequate remediation design and implementation

“define the problem before the solution”

II
Identification of Methane Sources

What types of scenarios would the LEA encounter?

LANDFILL

+

- **Common (Most Likely)**
- **Rare (Not Likely)**

Most Common Sources

Sources that generate CH_4 in high enough volumes and pressures to generate a migrating plume through soils

{FUGITIVE METHANE}

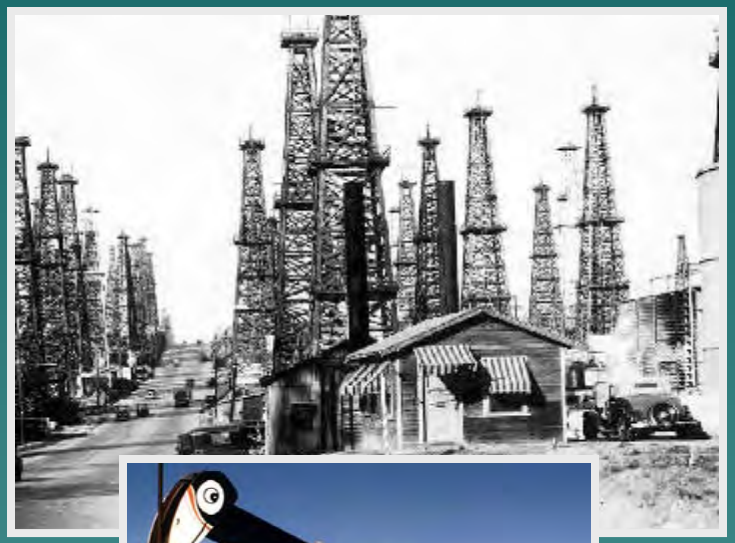
(Gas that you would see in your probes)

Natural Gas Leaks (Pipeline Gas)

Transportation Lines

Residential/Commercial Supply Lines

Naturally Occurring Methane
(Thermogenic/Petrogenic Gas)



Active / Abandoned Well Leaks

Natural Seepage (Underground Sources / Reservoirs)

Other Biogas (Swamp/Marsh Gas)

Decay of Organic Matter (CH_4 Formation) & Seepage Through Soil

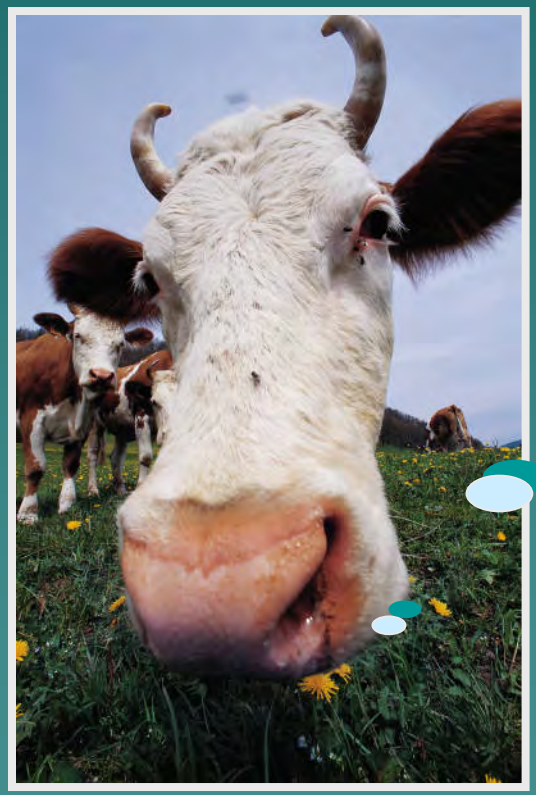
Other Sources
(Less Common/Not Likely)

- Low Potential – Underground Migrating Plumes
- Not Enough Documented Data (CH_4 Migrating-Problems)

(Gas that you wouldn't likely see in your probes)

- **Sewer Lines/Systems** (accumulation @ enclosed spaces)
- **Coal Mines**
- **Rice Fields**
- **Termites**
- **Oceans**
- **Livestock**

Factoid Livestock



Got Gas?

A cow can belch up to ½ lb of CH_4 / Day

\+

Sheep

Goats

Buffalo

Camels

Can Do It Too

Factoid Livestock

97.1 Million Cattle in the US

DO THE MATH!

48.5 Million lb CH_4 / Day

Got Gas?

An untapped source of energy

Not For Every Landfill in CA

- ➢Be Informed
- ➢Do your Homework

There are tools available!

San Diego

Oil & Gas Fields in CA

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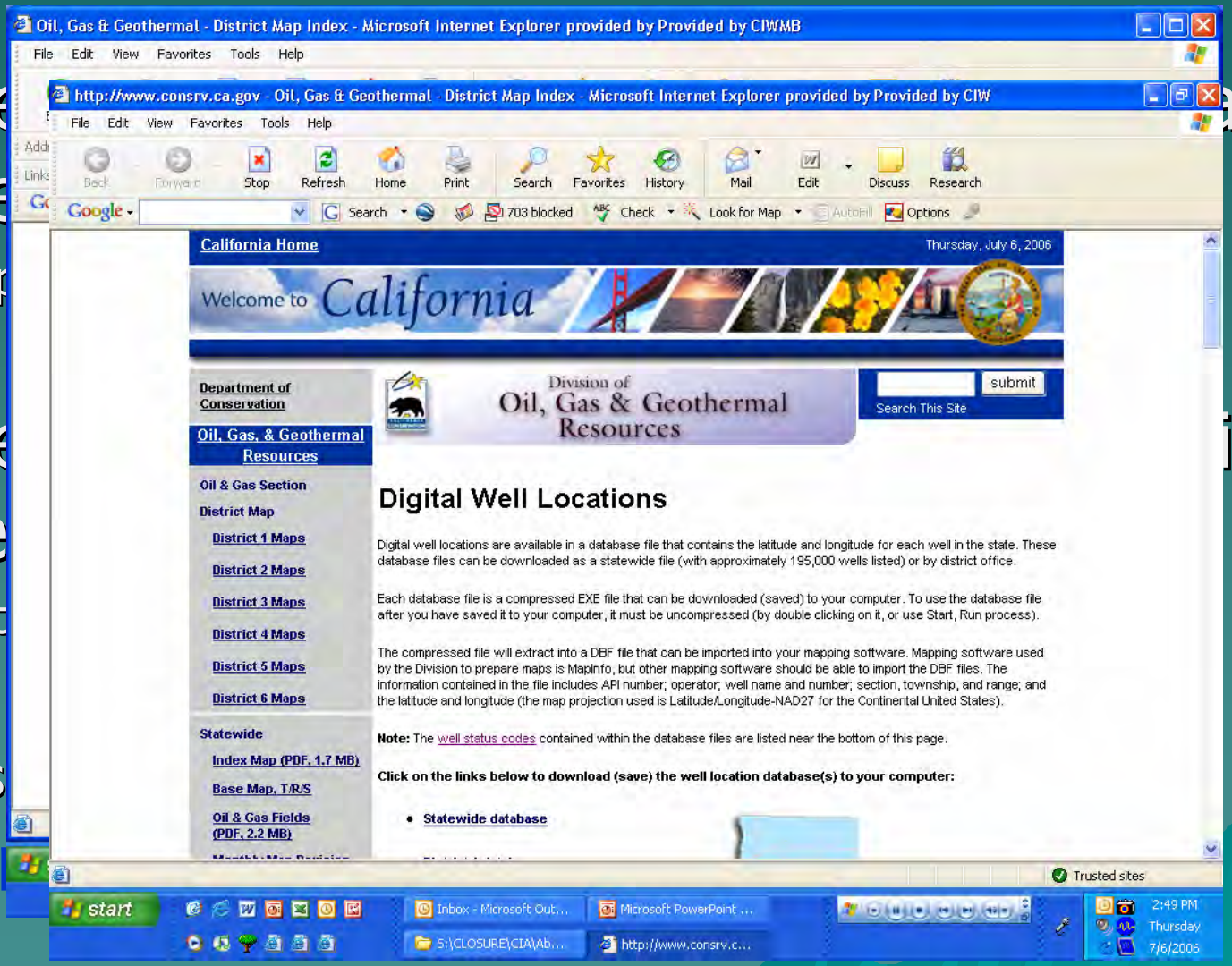


Oil Production in CA
3 Major Regions

- Kern County Region (69%)
- Los Angeles Basin Region (Central LA – Long Beach) (~10%)
- Outer Continental Shelf (Offshore 10.2%)

Kern
SL Obispo
Los Angeles
Ventura
Monterey
Orange

Forensics
Correlating CH_4 Releases to their Source

III
Analytical Procedures/Methods

Analytical Procedures/Methods

Fingerprinting Gas Releases (Gas Geochemistry)

Groups:

1. **Looking at the Various Constituents**
   - BTEX
   - H_2S
   - C_2+
   - Fixed Gases
   - Chlorinated Hydrocarbons/VOCs
   - Mercaptans

2. Stable Isotope Composition

- Hydrogen Isotopic Ratio ($^{2}H/^{1}H$)
- Carbon Isotopic Ratio ($^{13}C/^{12}C$)

3. Radio Isotope Composition

- ^{14}C Concentration (Carbon Dating)
- ^{3}H Concentration

4. Measuring the Caloric Values

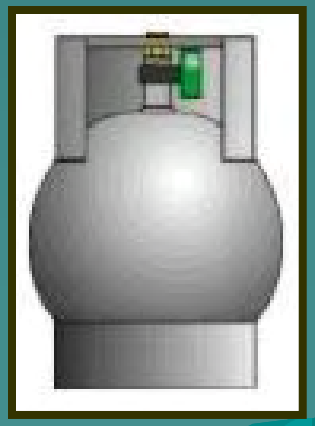
- CH_4 BTU value

Not an Easy Task!

Screening Process

Source x

Gas Probe



Landfill

Screening Process (contd.)

Formation Process

- LFG
- Swamp/Marsh Gas

Biogenic
Shallow depths/low temps
Anaerobic bacterial decomp
New Gas (0-100 years)

- Naturally Occurring
- Pipeline Gas

Thermogenic
High temps/depth/pressure
Thermal crack org. matter
Old Gas (Millions of years)

Elements for the ID of Sources

LFG

- CO_2 + CH_4 almost equal proportions
- VOCs/BTEX (trace)
- Low Oxygen
- H_2S (0-100 ppm) Note: 3-5% (US EPA)
- C_2-C_5 (trace)
- Unique Isotopic Fingerprinting ($^{13}C/^{12}C$ and $^{2}H/^{1}H$)
- ^{14}C Detected (Modern/New Gas)

Elements for the ID of Sources (contd.)

SWAMP / MARSH GAS

- Easily mistaken with LFG
- Same formation process (biogenic/anaerobic)
- No VOCs/BTEX
- No H_2S
- Unique Isotopic Fingerprinting ($^{13}C/^{12}C$ and $^{2}H/^{1}H$)

Elements for the ID of Sources (contd.)

NATURALLY OCCURRING GAS

- BTEX (trace)
- No VOCs
- H_2S Low–High (0.1 – 2.5%)/(0-98%)
- C_2-C_5 (up to 20%)
- Unique Isotopic Fingerprinting ($^{13}C/^{12}C$ and $^{2}H/^{1}H$)
- ^{14}C (Not Detected/Old Gas)

Elements for the ID of Sources (contd.)

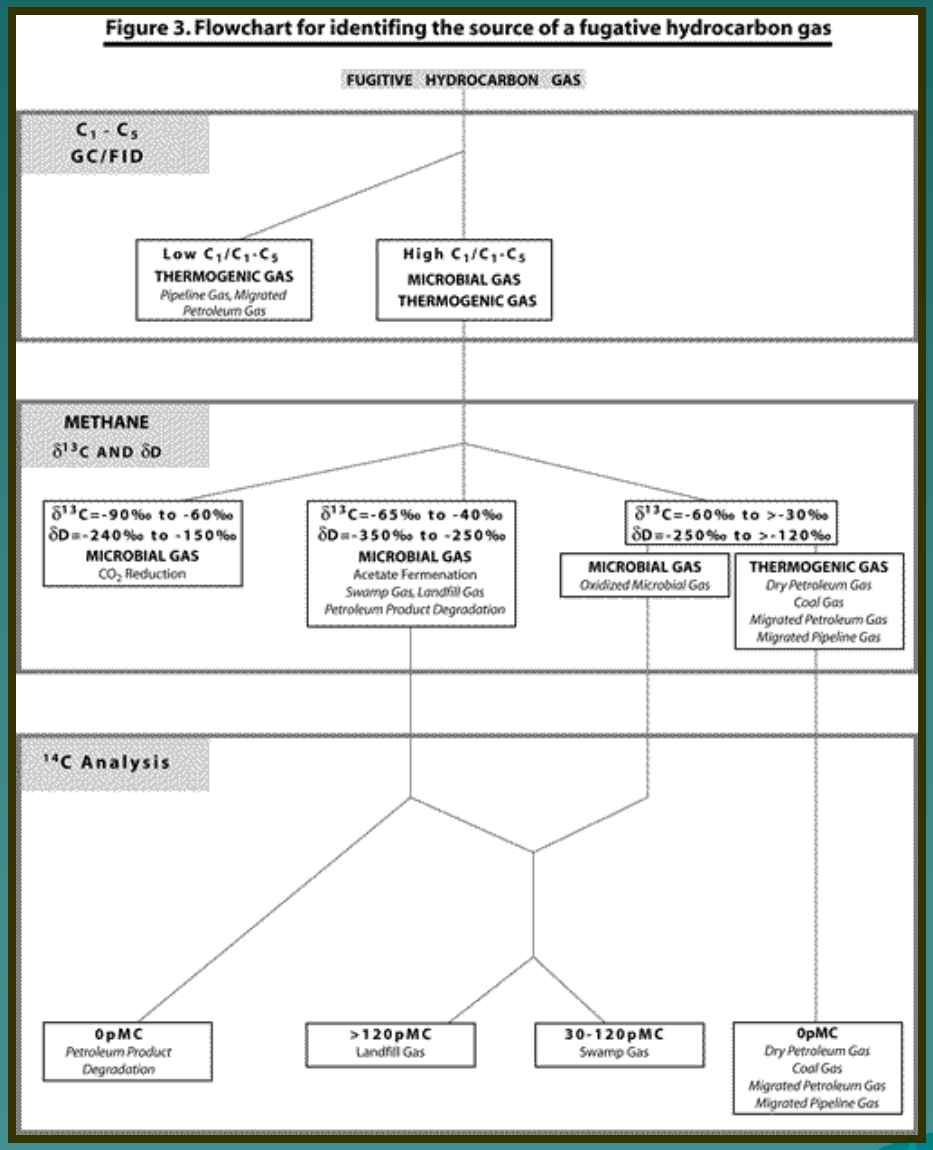
PIPELINE GAS

- Almost Pure CH_4 (80-90%)
- Some C_2-C_5 (%)
- Unique ID Element: Tracers (25-100 ppm)
  Mercaptans/Thiophene other Odorants

Forensics
Correlating CH_4 Releases to their Source

IV
Data Interpretation Techniques

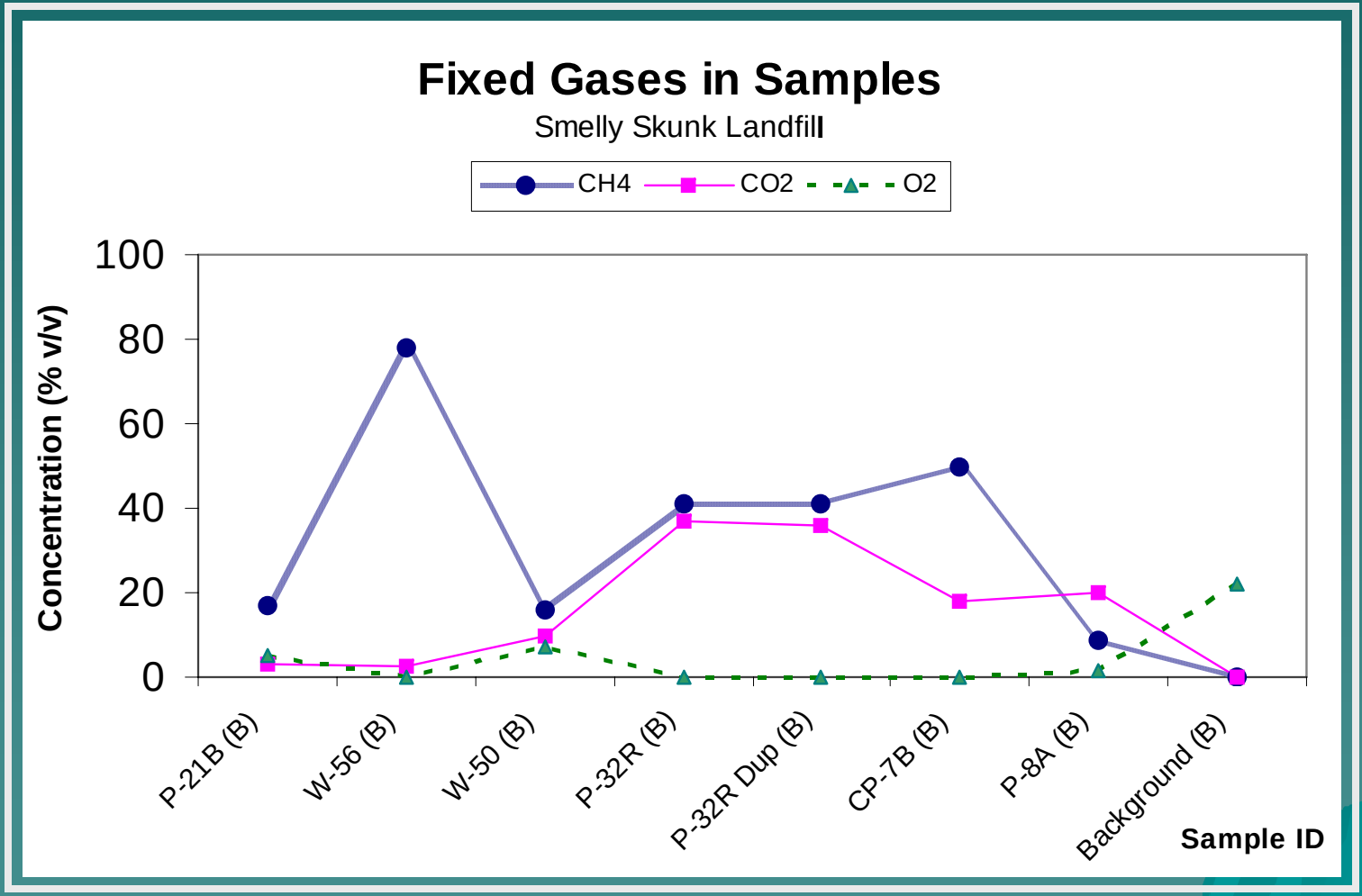
Data Interpretation



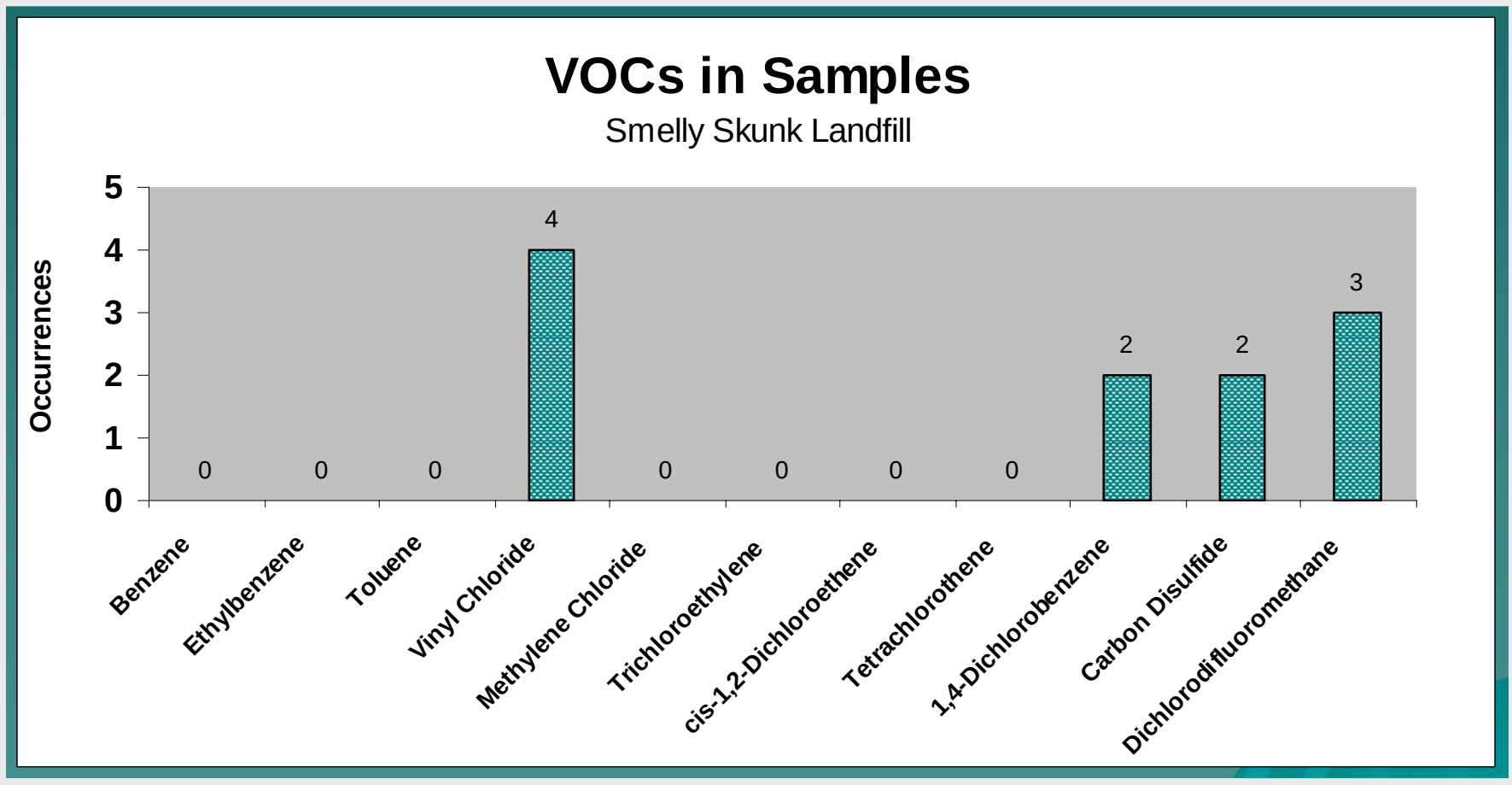
Tier Evaluation Process

Source's Unique ID ELEMENTS

Unique ID Elements



Unique ID Elements (contd.)



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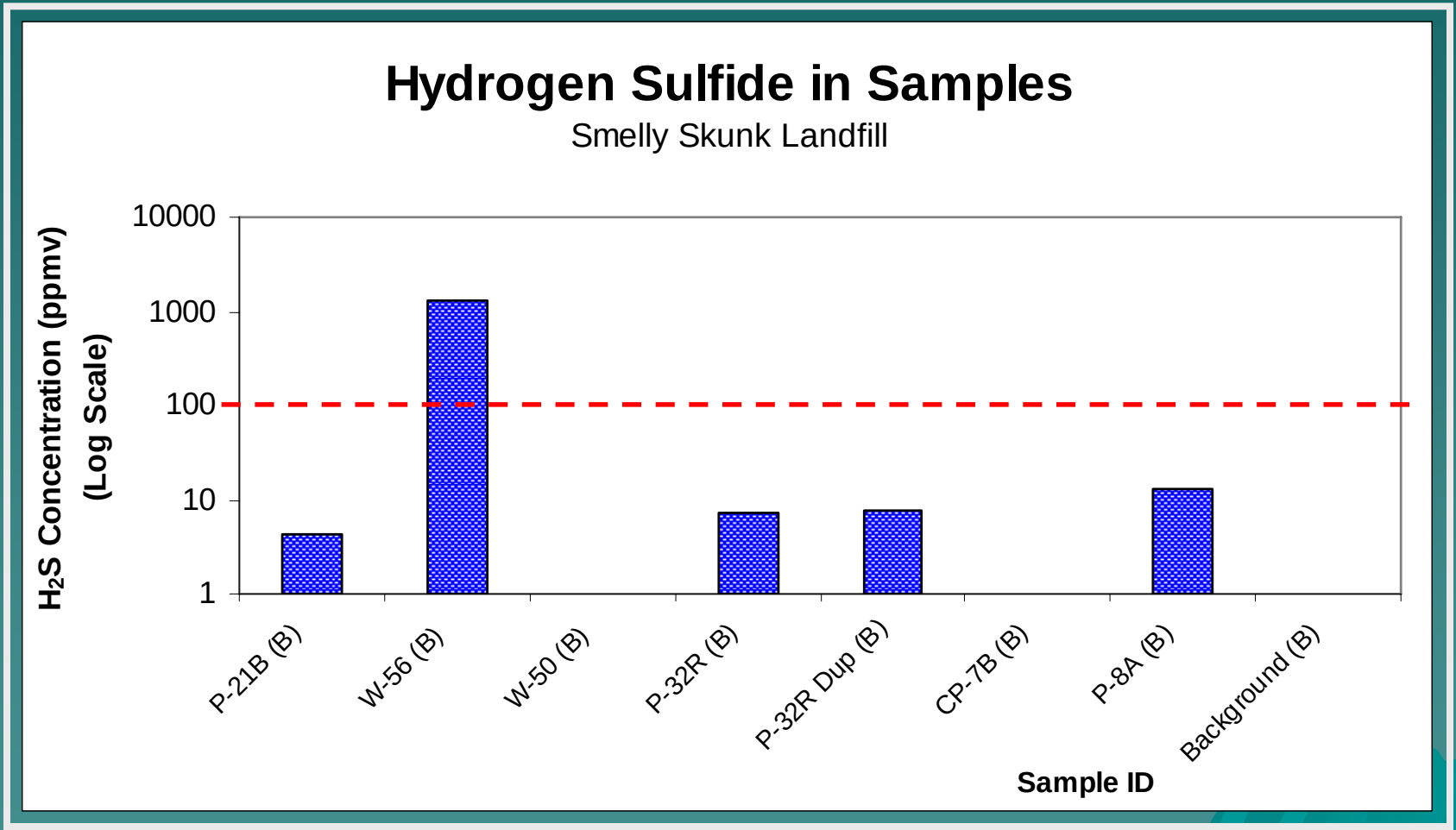

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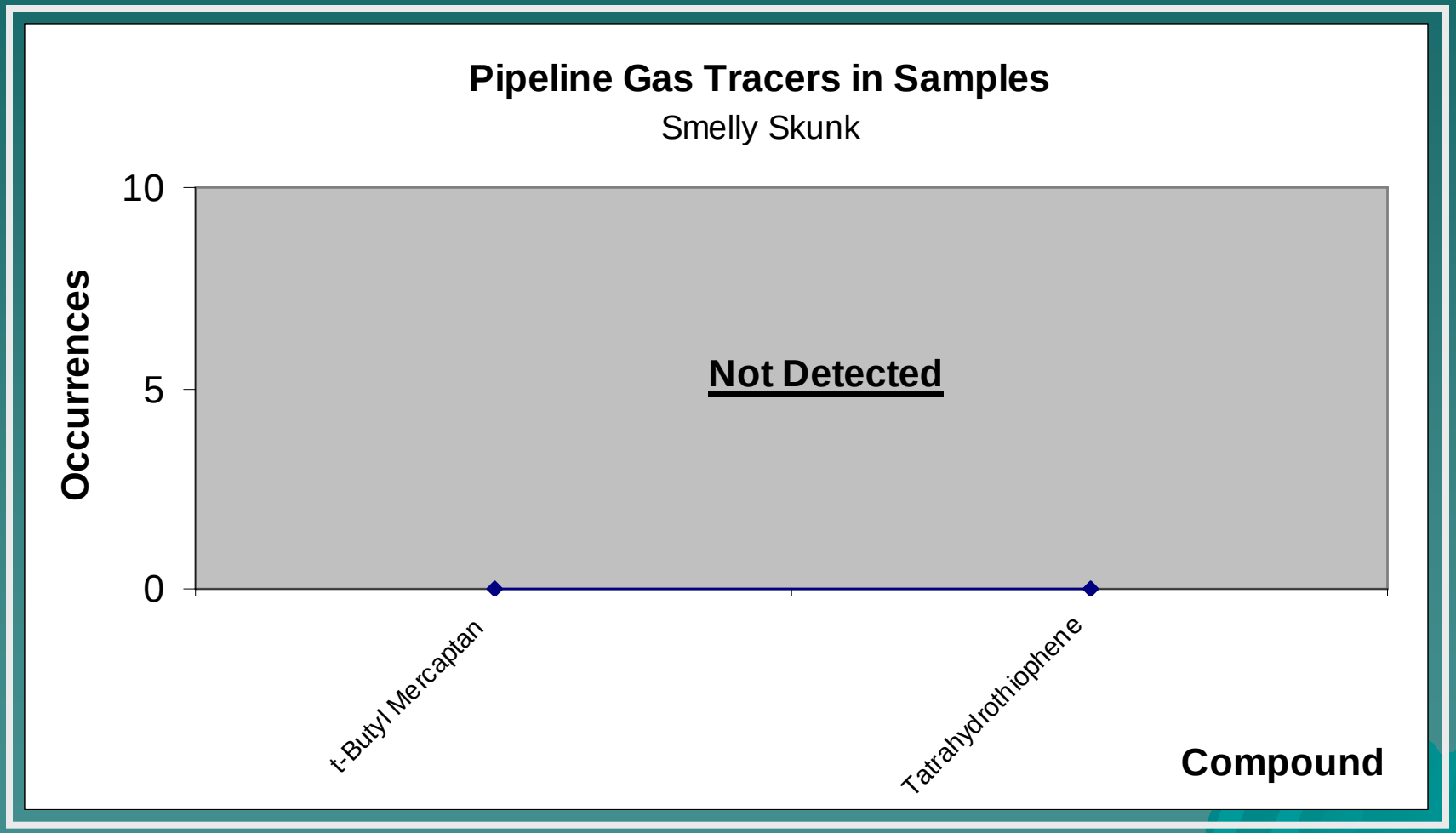
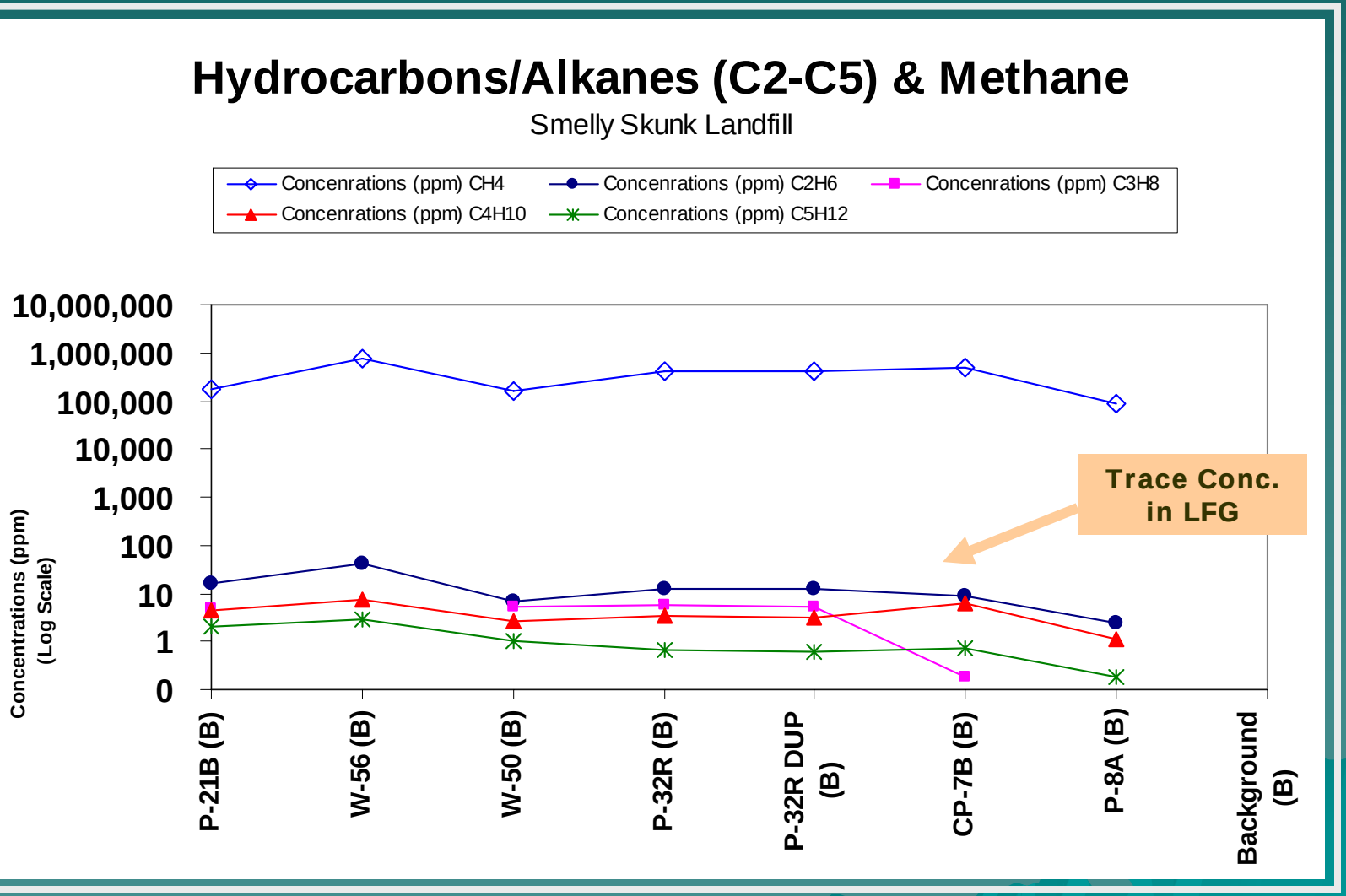


Unique ID Elements (contd.)



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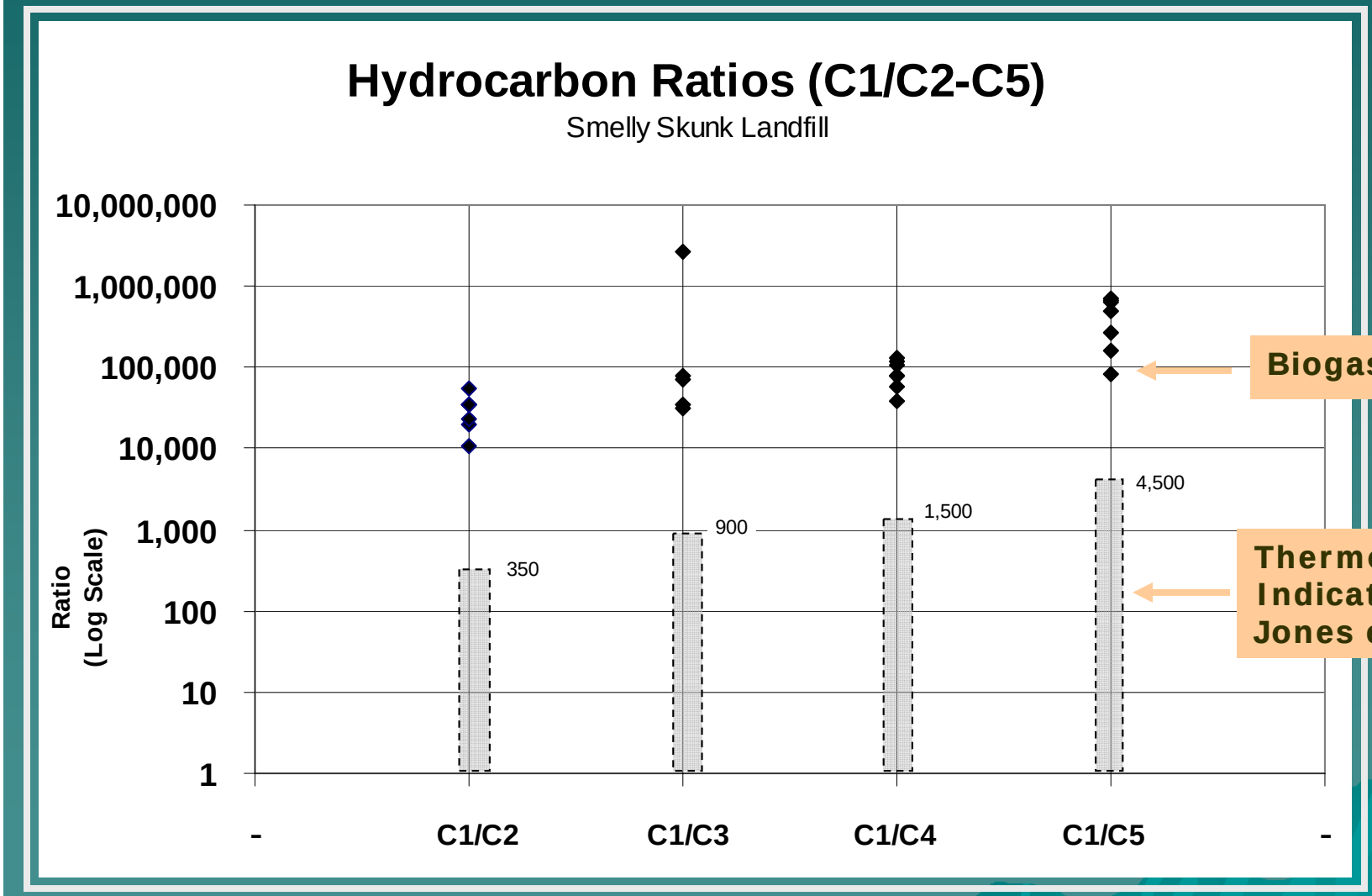


Sophisticated Geochemistry to ID Sources

Stable Isotope Composition

(Isotope Chemistry 101)

Naturally Occurring Isotopes:

^{12}C 98.89%
^{13}C 1.11%

} Same Element
Different Atomic Weight

^{1}H ~99.98%
^{2}H 0.0184%

} Same Element
Different Atomic Weight

The Principle of Employing Isotopes

Distribution of Isotopes

CH_4

Biogenic Methane Formation

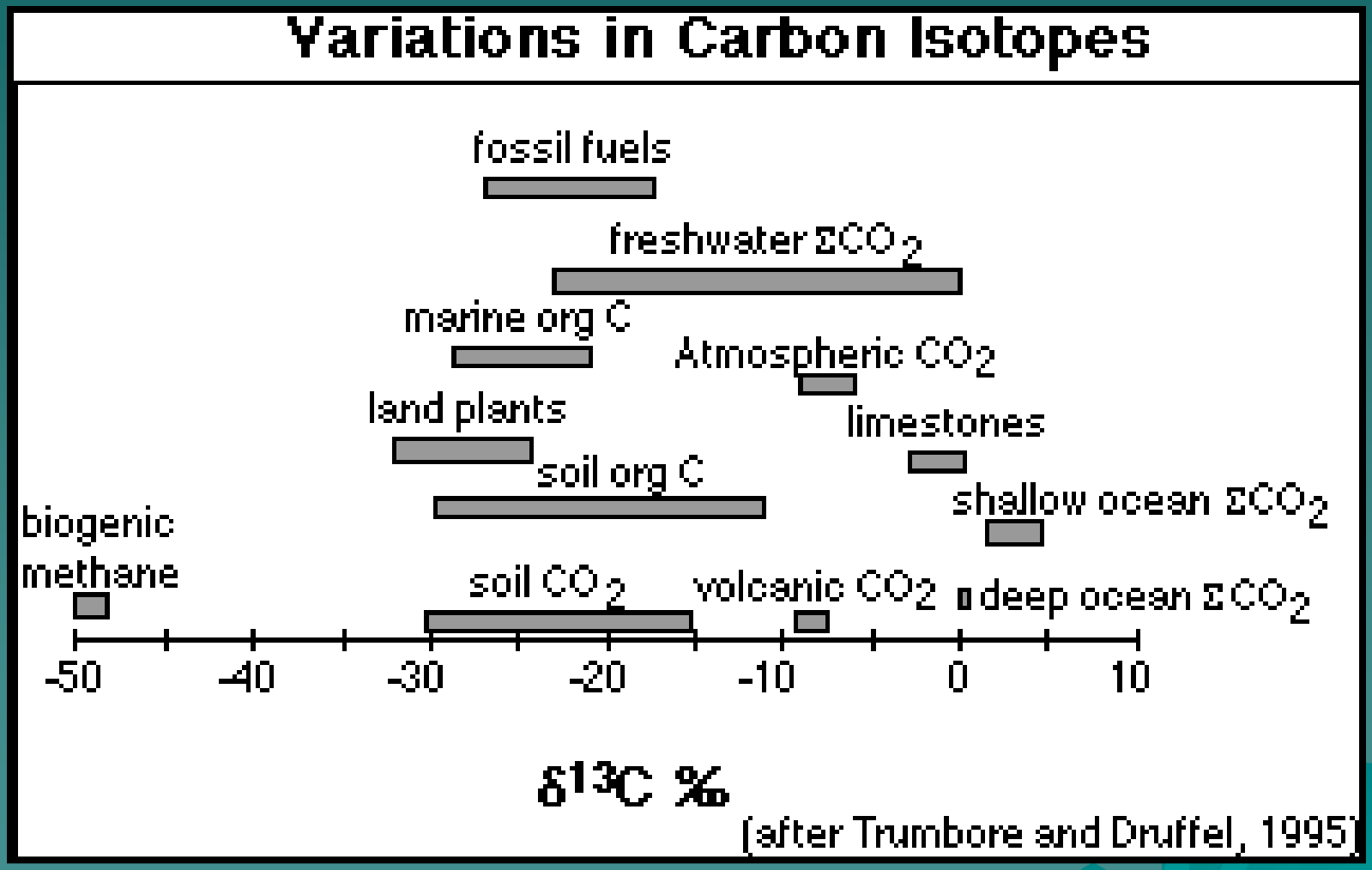
^{12}C
^{13}C

CH_3 -- |-- CO_2- + H a ⟹ **Bacterial Decomposition Light Isotopes ^{12}C & ^{1}H Preferentially Selected**

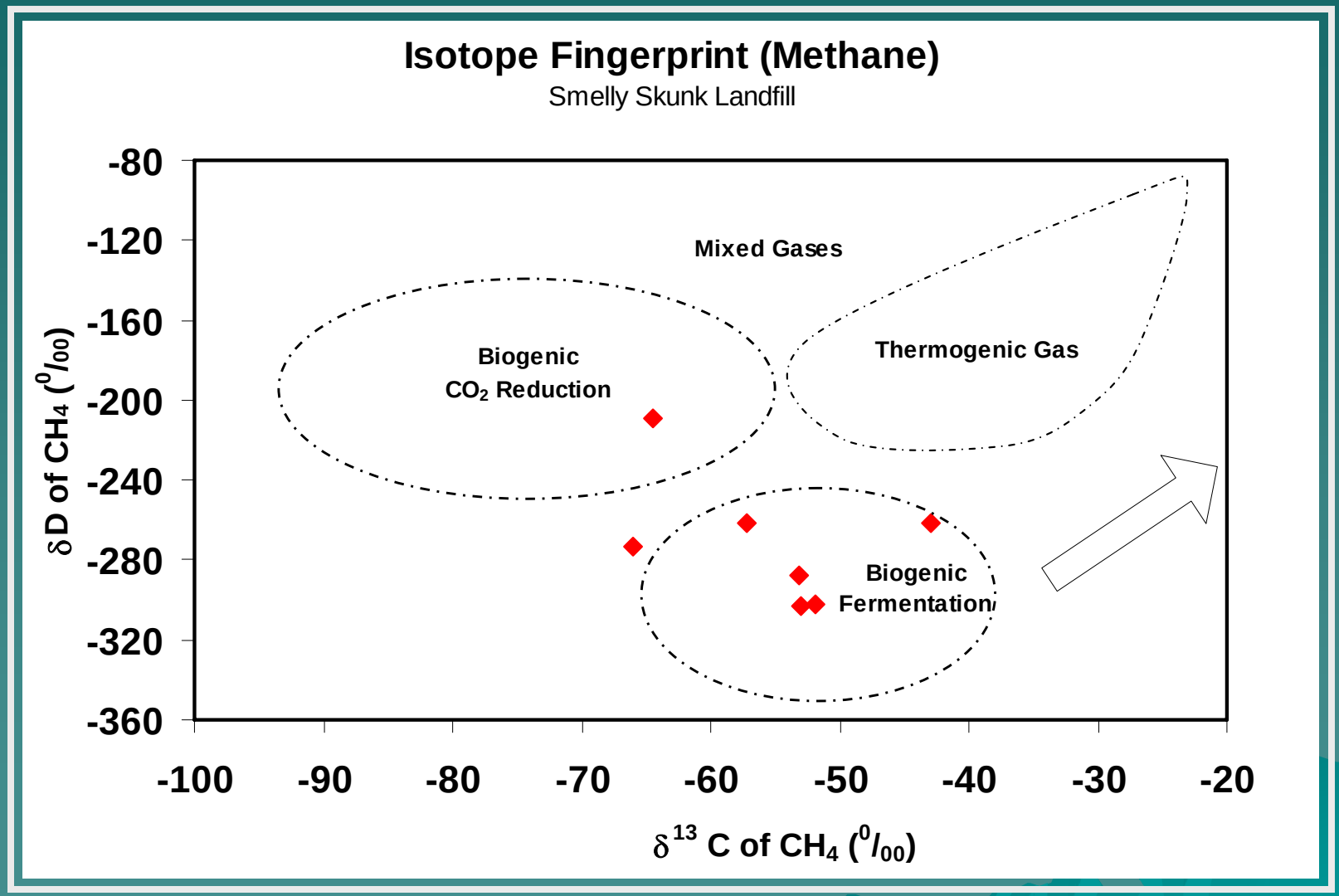
$CO_2 + 8H \Longrightarrow CH_4 + 2H_2O$

$^{13}C/^{12}C$ Ratio: Unique to the source
$^{2}H/^{1}H$ Ratio: Unique to the source

The Principle of Employing Isotopes



The Principle of Employing Isotopes



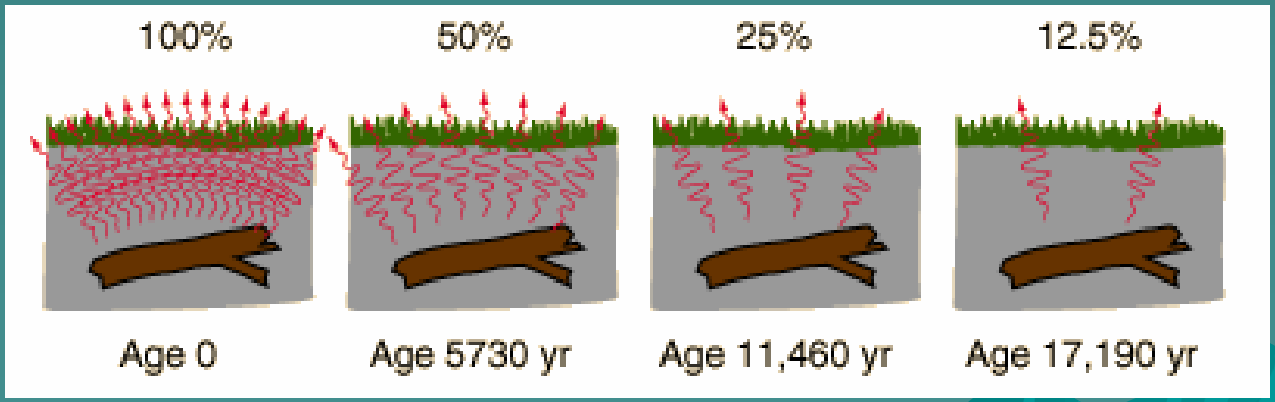
Radioisotope Composition

^{14}C Concentration – Carbon Dating

Naturally Occurring Isotopes:

^{12}C 98.89%
^{13}C 1.11%
^{14}C 0.0000000001% (Radioactive)

^{14}C Decays = Half-life 5730 yrs



How much ^{14}C is remaining in the CH_4?

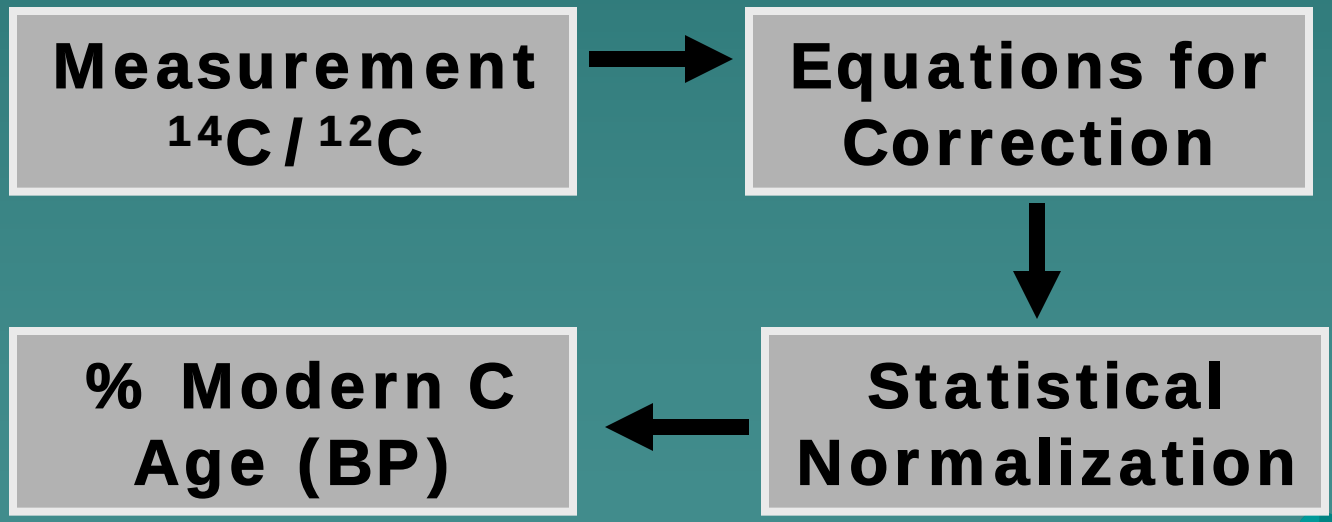
^{14}C Concentration – Carbon Dating

- Anything older than 60,000 years should have no detectable ^{14}C (thermogenic gas)
- If we detect ^{14}C, it is good evidence that gas was generated less than 60,000 years (landfill gas)

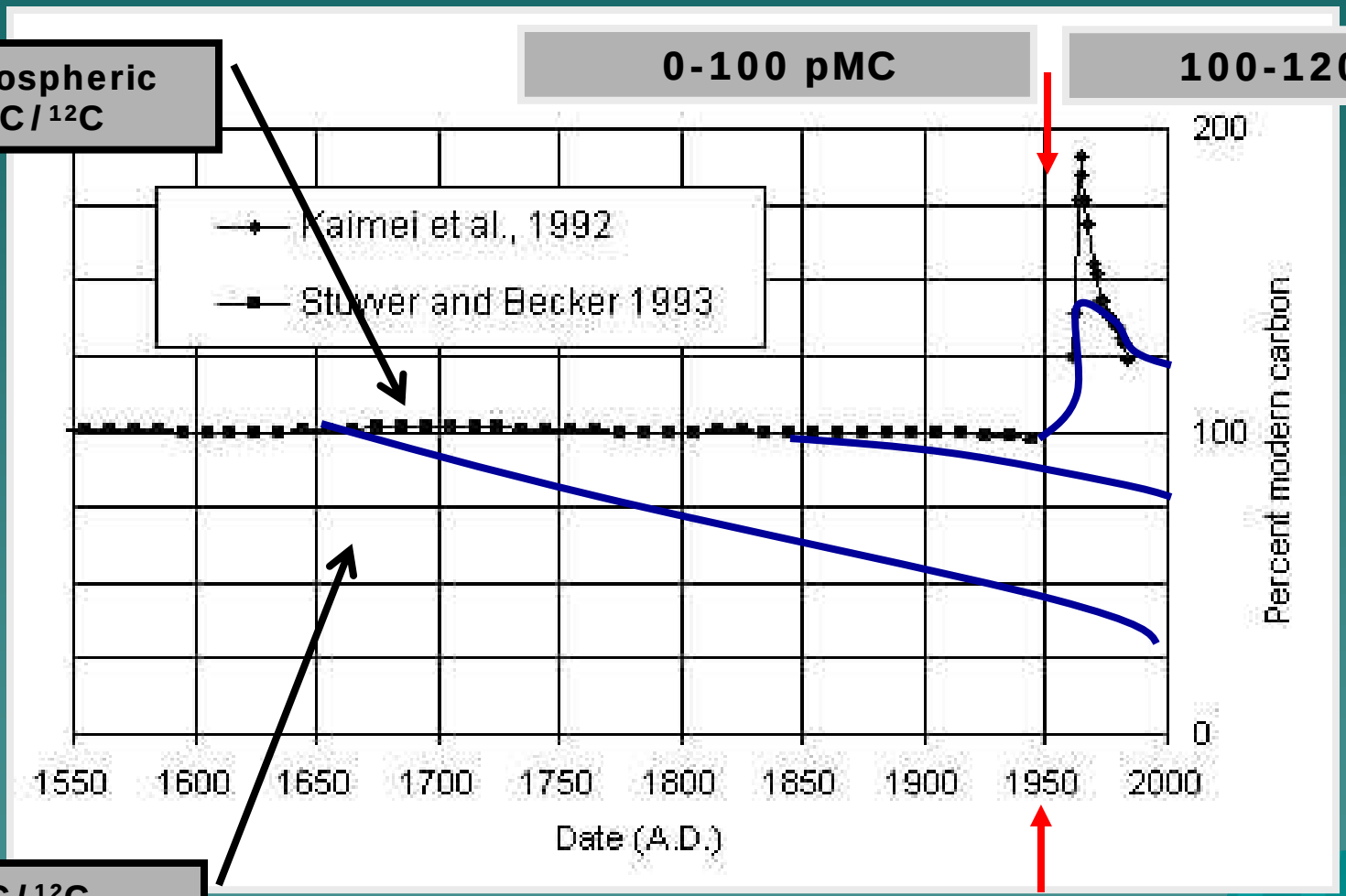
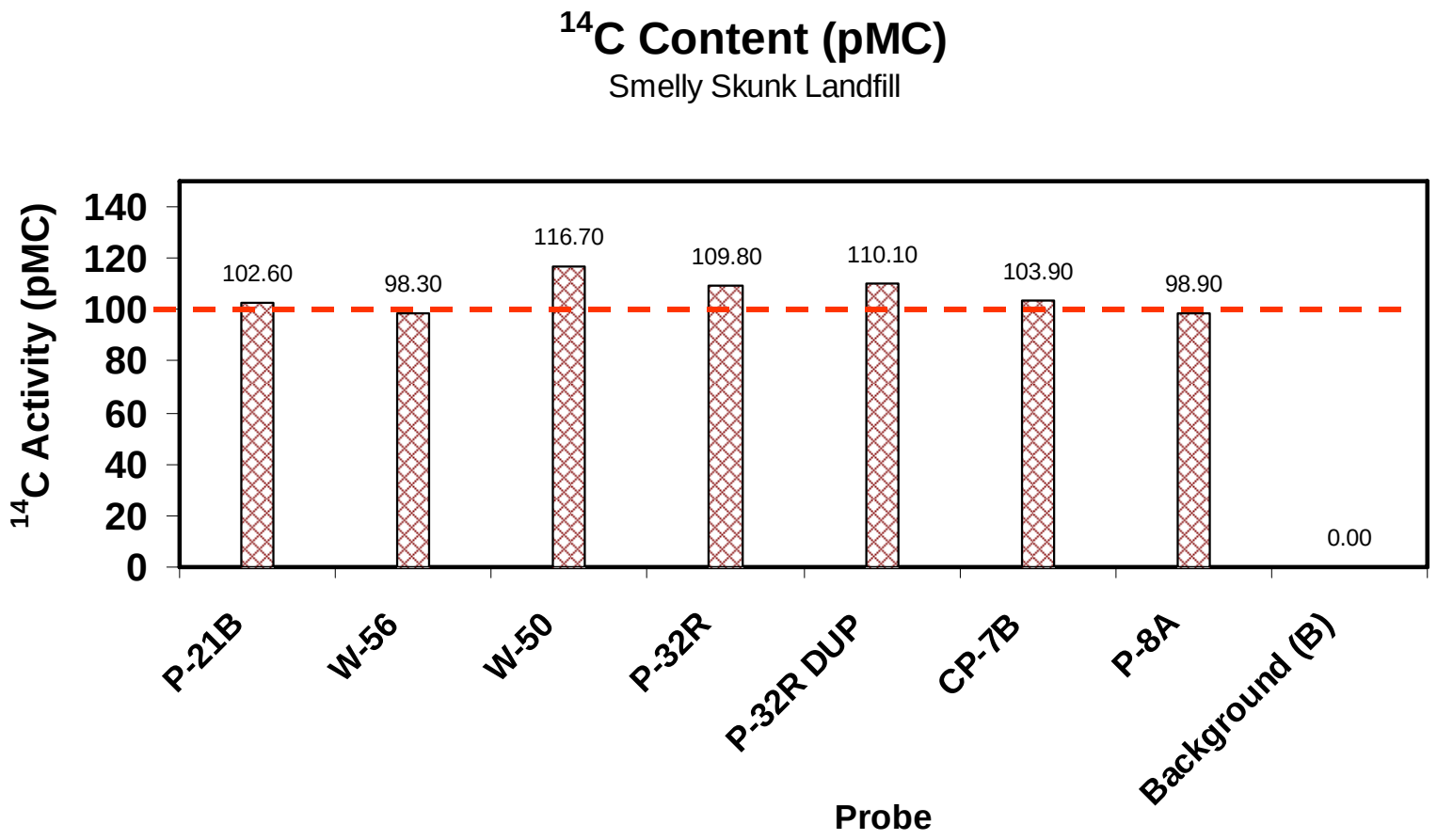
1. LFG <u>should</u> contain ^{14}C
2. Thermogenic gas <u>should not</u> contain ^{14}C

How is ^{14}C Measured

- Counting atoms/Accelerator MS
- AMS sophisticated - UCI & Livermore)



How is ^{14}C Measured



Reporting ^{14}C Results